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TEMPLATE SYNTHESIS OF METAL COMPLEXES CONTAINING NEW MACROCYCLIC LIGAND SYSTEMS

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The synthesis of macrocyclic metal complexes has been effected by the metal template condensation of various diamino-bisbenzaldehydes[1], oxamido-bisbenzaldehydes[2], pyridine-2,6-dicarbonyl compounds[3] with diamines or triamines in the presence of suitable metal salts.

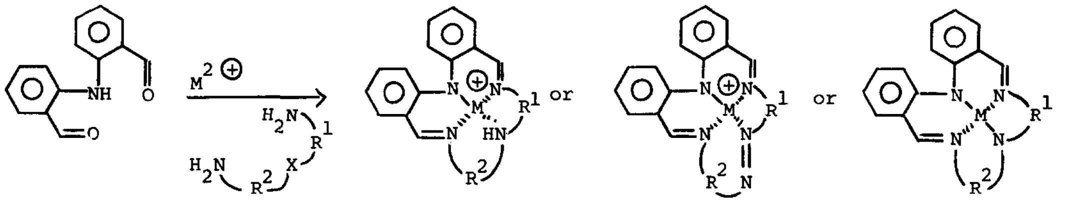
We now report that 2,2'-iminobisbenzaldehyde[4] (1) provides a very significant extension to the range of macrocyclic systems currently available. Nickel(II), cobalt(II) and copper(II) complexes (3a-h) can be prepared readily in good yield by combination of the dialdehyde (1), the appropriate metal salt and the amines (2a-h) respectively in refluxing methanol or ethanol for several hours (Scheme 1). Several comparisons with macrocyclic complexes derived from pyridine-2,6-dicarbonyl compounds e.g. (4) are relevant. Deprotonation of the amino proton derived from (1) occurs in all complexes (3) and thus both neutral complexes (3e-g)and cationic complexes (3a-d) can be prepared. These contain fourteen- to sixteen-membered rings. The structural moiety provided by (1) is much more flexible than that provided by pyridine-2,6-dicarbonyl compounds and six-membered rather than five-membered chelate rings are incorporated into the resulting planer complexes. This flexibility thus gives rise to the formation of complexes which range from essentially flat structures e.g. (3e) to severely buckled structures, e.g. (3g), as shown by molecular models and electronic spectra.

The additional new macrocyclic complexes (5b-g) can be obtained by reaction of the amines (2b-g) with 2,6-diacetyl pyridine (4) and nickel(II), copper(II) or cobalt(II) salts. Complexes (5b) are already well-known[3]. It is of special interest that nickel(II) and copper(II) (but not cobalt(II)) complexes (5e) can be formed. These complexes contain twelve-membered rings presumably stabilised by full conjugation. The related more-saturated twelve-membered macrocyclic complexes cannot be obtained[5] from the corresponding aliphatic triamine (2a).

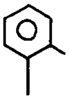
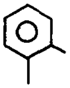
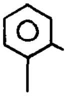
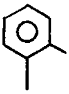
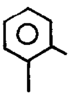
Furthermore, macrocyclic quinquedentate complexes of copper(II) and zinc(II) can be formed similarly by combining the tetrafunctional amine (6) with the dialdehyde (1).

References

1. D.St.C. Black, A.J. Hartshorn, M. Horner and S. Hünig, Aust.J.Chem., 30, 2493 (1977) and earlier papers cited therein.
2. D.St.C. Black, C.H. Bos Vanderzalm and A.J. Hartshorn, Inorg.Nucl.Chem.Letters, 12, 657 (1976).
3. R.H. Prince, D.A. Stotter and P.R. Woolley, Inorg.Chim.Acta, 9, 51 (1974) and earlier papers cited therein.
4. E.D. Bergmann, M. Rabinovitz and I. Agranat, Bull.Res.Council Israel, 11A3, 149 (1962).
5. R.L. Rich and G.L. Stucky, Inorg.Nucl.Chem.Letters, 1, 61 (1965).



(1) (2a-g) (3a-c) (3d) (3e-g)

2,3,5	a	b	c	d	e	f	g
R^1	$(CH_2)_2$	$(CH_2)_3$	 CH_2				
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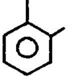
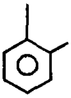
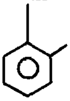
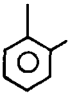
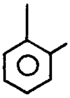
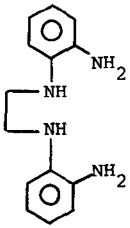
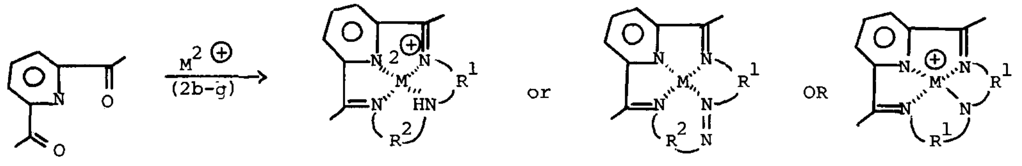
R^2	$(CH_2)_2$	$(CH_2)_3$	CH_2 				



(6)



(4) (5b,c) (5d) (5e-g)